

Preparation and characterization of a novel bioactive restorative composite based on covalently coupled polyurethane–nanohydroxyapatite fibres

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Abstract

Nanohydroxyapatite (n-HAp) was prepared using a sol–gel method. n-HAp powder was obtained from the gel form by heat treatment followed by grinding using ball milling. A novel polyurethane composite material was prepared by chemically binding the hydroxyapatite to the diisocyanate component in the polyurethane backbone through solvent polymerization. The procedure involved the stepwise addition of monomeric units of the polyurethane and optimizing the reagent concentrations. The resultant composite material was electrospun to form fibre mats. The fibres were less than 1 μm in thickness and contained no beads or irregularities. Chemical structural characterization of both the ceramics and the novel polymers were carried out by Fourier transform infrared and Raman spectroscopy. X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy and Brunauer–Emmett–Teller surface area analysis were also employed to observe the crystal lattice and size and surface area of the n-HAp. Further characterization (by energy-dispersive X-ray analysis and SEM) of the spun fibres revealed the presence of elements associated with hydroxyapatite and polyurethane without the presence of any loose particles of hydroxyapatite, indicating the formation of the covalent bond between the ceramics and the polymer backbone.

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1. Introduction

It is desirable for a restorative dental material to have bioactive and bonding properties at the interface between the material and the tissue to prevent micro-leakage and ingress of bacteria. Polymeric materials have been used in medical and surgical applications for a number of years [1]. The requirement of specific material differs according to the nature of the application, and there are different techniques in modifying and fabricating different compositions to achieve exact requirements for clinical use [2].

Polyurethane is a versatile class of polymers and is one of the most interesting classes of synthetic elastomers with unique properties that are used in a broad range of applications due to their excellent physical properties and relatively good biocompatibility [3].

A great deal of attention has been given to the synthesis, morphology, chemical and mechanical properties of this family of materials [4]. Polyether-type polyols possess good physical strength, abrasion resistance, water resistance, fatigue life and biocompatible character [5]. Research on polyurethane has focused on its potential application as a facial prosthesis in dentistry, based on its inherent environmental stability, high tear resistance and low modulus without the use of plasticizer, and good ultimate strength and elongation. This material can accept intrinsic colouring

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and is amenable to maxillofacial processing techniques [6–8]. Polyether-based impression materials have been used in restorative dentistry to record intra-oral structure for fabrication of definitive restorations [9]. Urethane-based resins (UDMA) are available for light-activated material formulated specifically for fabrication [10,11].

Nanohydroxyapatite (n-HAp) has been proved to be an osteoconductive material [12] that also binds chemically to enamel and dentine. A significant characteristic of bioactive material is the ability to bond with living tissue through the formation of a hydroxyapatite interfacial layer [13]. From a biological viewpoint, combination of polymer and ceramic material to fabricate a bioactive composite scaffold is a natural strategy. From the material science perspective, a single material type is not able to provide the necessary mechanical and chemical properties required for biomedical applications [14]. Hence, in recent years, considerable attention has been focused towards the development of polymer composites to fulfil the required properties for biomedical applications. The significance of using a composite material is that, through the amount and type of reinforcing material, the mechanical and biological properties can be tailored for each specific application. It has been reported that various polymers, such as polylactic acid, polyglycolic acid, poly- ϵ -caprolactone, polyethylene, polyetheretherketone and polyurethane, have been used with HAp as composite materials [15–22]. The interface adhesion of HAp particles and the polymer matrix is a major factor affecting the properties of the composites [23,24]. Surface modification by surface adsorption and grafting of HAp to polymers provide an effective way to manipulate the surface properties of HAp [15]. When nanoparticles (n-HAp) and polymers form a composite, provided that homogeneous dispersion of the nanoparticles is achieved at the microscopic level, the mechanical properties are expected to be improved and/or new, unexpected features might appear [5]. Liu et al. [23] and Dong et al. [25] studied the reactivity of isocyanate with hydroxyapatite and calcium hydrogenphosphate (CaHPO_4 , CHP) respectively. They observed that there was a covalent linkage between isocyanate and HAp, and a urethane linkage between hexamethylene diisocyanate (HMDI) and CHP, showing that the hydroxyl ($-\text{OH}$) groups at the surface of n-HAp have reactivity towards organic functional groups.

Electrospinning is a relatively new process for developing nanofibres. It allows the continuous production of fibres ranging from submicrometres to nanometres [26]. In this process, continuous filaments are drawn from a liquid polymer or melt through a spinneret by high electrostatic forces and later deposited on a conductive collector [27,29].

Due to the high-surface-area to volume ratio of the electrospun fibres and the high porosity on the submicrometre length scale of the obtained non-woven mat, proposed applications for these materials include nanofibre-reinforced composites, nanofibre supports for enzymes and

catalysts, and nanofibrous membranes in biomedical applications for drug delivery, wound healing, cardiac grafts, guided bone regeneration and scaffolding for tissue engineering. Electrospun fibres mats are suitable for use as scaffold because of their highly porous three-dimensional (3-D) structure [29–34]. The morphology of electrospun fibres depends on a number of factors, including viscosity, conductivity and surface tension, hydrostatic pressure in the capillary, electric potential at the tip, distance between the tip and the collector, and ambient parameters, including temperature, humidity and air velocity in the electrospinning chamber [26,30,35].

Various polymers, such as polymetaphenylene-isophthalamide, polyetherimide, polyethylene oxide, polyethylene terephthalate, polyaniline, polycaprolactone and poly-L-lactic acid, have been successfully electrospun into nanofibres [25,28,36–38]. A few studies have reported the culture of chondrocytes and osteoblasts on polycaprolactone [33,34]; in addition, the incorporation of calcium carbonate or HAp has also been reported [29,32,34,39]. It was reported that the presence of non-interactive rigid particles increased the shear viscosity of dilute suspension and decreased the conductivity of the resulting mixture. It was also observed that beaded fibres were obtained; however, this depends mainly on the concentrations of the polymer and particles [32,34]. The resin-based dental polymers 2,2'-bis-(4-(methacryloxypropoxy)-phenyl)-propane and triethyleneglycol-dimethacrylate have been investigated with the reinforcing effect of electrospun nylon 6 nanofibres [40]. It was found that the fibres have a crystalline structure and are mechanically strong. The small diameter of nanofibres also provides a high ratio of surface area to volume, which could enhance the intermolecular hydrogen bonding between the filler of nylon 6 nanofibres and the matrix of resin polymers. Electrospinning is the technique used to deposit the particles onto the surface. The basic principle of electrospinning is the generation of a spray of charged, micron-sized droplets. This is done by means of electrostatic atomization. The sprayed droplets are directed towards a heated substrate as a result of an applied potential difference [41].

In this study, a novel bioactive composite material based on covalently linked polyurethane and nanohydroxyapatite particles was synthesized and characterized. The composite was also electrospun to produce nanofibres for morphological characterization.

2. Materials and methods

2.1. Materials and synthesis of hydroxyapatite

n-HAp was synthesized by ammonium hydrogen phosphate 98% ($(\text{NH}_4)_2\text{HPO}_4$) and calcium nitrate tetrahydrate 99% ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) as phosphate and calcium precursors, distilled water and ethanol were used as solvent for precursors respectively. Ammonium hydroxide was used to control the pH value. All materials were purchased from

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